Influence of Salt Bed of the Zawada Basin on Mine Waters in the Upper Silesian Coal Basin (Poland)

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Abstract
This paper presents the isotopic compositions ($\delta^{34}$S, $\delta^{18}$O) of sulphates in mine waters of all coal mines neighboring the region of the Zawada Basin in the Upper Silesian Coal Basin (Poland). In mine waters from the Miocene of the Chwałowce Coal Mine and from the Carboniferous Formations of the Dębieńsko Coal Mine sulphates have typical isotopic composition of the evaporites in the Badenian and salt bed of the Zawada Basin. Isotopic data of sulphates in other mine waters from the Carboniferous formations of the Bolesław Śmialy, Budryk, Chwałowice, Jankowice coal mines are different. Studies of the origin of sulphates confirmed the influence of salt bed on the mine waters in the north-western side of the Zawada Basin in the Dębieńsko Coal Mine and probably also should be in the Paruszowiec region where the potential sources of coal are present.

Key words: sulphates, isotopic composition, salt bed, mine waters

Introduction
The decade of the 90's last century was characterized by restructuring of the mining industry and closures of coal mines of the Upper Silesian Coal Basin (USCB) due to costly exploitation at very deep levels. Now, new regions of the USCB are being surveyed as potential sources of coal. The region of Paruszowiec is one of these areas. In this western region of the USCB rich and relatively shallow levels of coal occur. However, the important factor hindering the exploitation is the forecast of possible hazards originating from the geological structure and hydrogeological conditions. In the Paruszowiec region tectonic complexity, and the weathering zones at the top of the Carboniferous formations occur. At the upper most strata, in the Miocene, salt deposits of the Zawada Basin are present. Many papers have been published so far with the discussion on the influence of the salinity waters from the Miocene on the occurrence in the Carboniferous formations (Michael 1913; Rosłoński 1933; Konior 1958). The discussion intensified after Rożkowski and Rudzińska-Zapaśnik (1983) found the abnormally high mineralization of 351 g/dm$^3$ at the 495 m deep level in the Budryk Coal Mine (CM). A. Rożkowski (2001) estimated that the area of the influence of the salt bed from the Zawada Basin is about 200 km$^2$.

Dissolution of salt, gypsum into waters may lead to significant inflow of brines, as well as changes of mechanical properties of rocks affecting the exploitation of coal in the mine workings. Therefore, in order to assess correctly perspectives of the coal mining in the Paruszowiec region, it is necessary to determine the impact of waters from the Miocene of the Zawada Basin on the mining process. The aim of this paper is to present results of isotopic composition of sulphates in waters flowing into all coal mines, located of neighboring region and surrounding the Zawada Basin. Waters were taken from the Bolesław Śmialy, Budryk, Dębieńsko, Chwałowice, Jankowice, Żory and Krupiński coal mines. The measurements of $\delta^{34}$S and $\delta^{18}$O in mine waters may give some information on the origin and on the source of sulphates.

Sampling and analyses
The region being studied consists of the following coal mines: Bolesław Śmialy, Budryk, Dębieńsko, Chwałowice, Jankowice, Żory and Krupiński, and is situated in the western and central part of the USCB. In this area the Carboniferous formations are covered by the Miocene, Quaternary and locally Triassic deposits.

Water samples were filtered and sulphates were precipitated as BaSO$_4$ by BaCl$_2$ solution acidified with HCl. The isotopic composition $\delta^{34}$S and $\delta^{18}$O were analyzed by mass spectroscopy on SO$_2$ and CO$_2$ gases, respectively. SO$_2$ was extracted from BaSO$_4$ by the method developed in the Mass Spectroscopy Laboratory of the Maria Curie-Skłodowska University (Lublin) (Halas, Szaran 2001),
whereas CO$_2$ was prepared by the method described by Mizutani (1971). The concentration of sulphates was determined by the gravimetric method.

**Isotopic composition in the Miocene minerals**

In the majority of the Badenian evaporities present in Poland, and in the world as well, the isotope compositions of sulphur ($\delta^{34}$S) varies from +18.0‰ to +25.7‰, while the isotopic compositions of oxygen ($\delta^{18}$O) from +10.1‰ to +17.7‰ (Claypool et al. 1980; Halás et al. 1996; Bukowski, Szaran 1997; Kasprzyk 1997; Pyer et al. 2002). The isotopic data of the marine minerals in the salt bed of the Zawada Basin sampled from the Chwałowice Coal Mine are $\delta^{34}$S = +24.55‰ and $\delta^{18}$O = +12.24‰ also agree well with these values. Similarly, isotopic composition $\delta^{34}$S = +21.17‰ and $\delta^{18}$O = +13.90‰ in the gypsum from the Miocene in the Szczyciogłowice CM was found.

**Isotopic composition of sulphates in mine waters of the Bolesław Śmialy CM**

The isotopic data and the concentrations of sulphates in mine waters of the Bolesław Śmialy CM are presented in Table 1.

<table>
<thead>
<tr>
<th>Number of sample</th>
<th>Sampling level</th>
<th>$\delta^{34}$S [‰]</th>
<th>$\delta^{18}$O [‰]</th>
<th>$\text{SO}_4^{2-}$ [mg/dm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>420 m</td>
<td>+3.02</td>
<td>+1.86</td>
<td>895</td>
</tr>
<tr>
<td>2</td>
<td>530 m</td>
<td>+30.67</td>
<td>+15.41</td>
<td>1110</td>
</tr>
</tbody>
</table>

The mine waters flowing into the Bolesław Śmialy Coal Mine contain sulphates. These sulphates have two different isotopic data. Sulphur in sulphates of the mine water from level 420 m has the value of $\delta^{34}$S = +3.02‰ with respect to sulphur from the Carboniferous strata (Pluta 2002) and similar to atmospheric sulphates which is mainly formed from organic matter during the combustion of fuels. In accordance with these results, sulphates in mine water from level 420 m were formed by the sulphides or the organic matter oxidation processes.

Sulphates in mine water flowing on level 530 m have the following isotopic data: $\delta^{34}$S = +30.67‰ and $\delta^{18}$O = +15.41‰. These very high values have been found in evaporites of Cambrian age and halite and gypsum of the early Triassic – Roet in the Netherlands, Germany, Austria (Klaus, Pak 1974; Pilot et al. 1972) and also in Poland (Kovalevych et al. 2002). Probably the evaporites of the early Triassic – Roet were dissolved into the mine waters of the Bolesław Śmialy Coal Mine on the level 530 m.

**Isotopic composition of sulphates in mine waters of the Dębienisko CM**

The isotopic data and the concentrations of sulphates in mine waters of the Dębienisko Coal Mine are presented in Table 2.

<table>
<thead>
<tr>
<th>Number of sample</th>
<th>Sampling level</th>
<th>$\delta^{34}$S [‰]</th>
<th>$\delta^{18}$O [‰]</th>
<th>$\text{SO}_4^{2-}$ [mg/dm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>600 m</td>
<td>+23.97</td>
<td>+11.10</td>
<td>1470</td>
</tr>
<tr>
<td>2</td>
<td>690 m</td>
<td>+24.77</td>
<td>+11.58</td>
<td>1570</td>
</tr>
</tbody>
</table>

Sulphates in mine waters of the Dębienisko CM are easy to identify because their $\delta^{34}$S and $\delta^{18}$O values are characteristic for the sulphate minerals of the Badenian deposits. These sulphates are contained in the evaporites in salt bed of the Zawada Basin. The measurements of isotopic composition of sulphates give information on the influence of marine deposits on the occurrence in mine waters of the Dębienisko CM.
Isotopic composition of sulphates in mine waters of the Budryk CM
The isotopic data and the concentrations of sulphates in mine waters of the Budryk CM are presented in Table 3.

Table 3 Isotopic composition and concentrations of sulphates in mine waters of the Budryk CM

<table>
<thead>
<tr>
<th>Number of sample</th>
<th>Sampling level</th>
<th>$\delta^{34}S$ [%e]</th>
<th>$\delta^{18}O$ [%e]</th>
<th>$SO_4^{2-}$ [mg/dm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>330 m</td>
<td>+40,80</td>
<td>+20,56</td>
<td>850</td>
</tr>
<tr>
<td>2</td>
<td>540 m</td>
<td>+32,36</td>
<td>+18,81</td>
<td>1990</td>
</tr>
<tr>
<td>3</td>
<td>540 m</td>
<td>+34,86</td>
<td>+19,56</td>
<td>1490</td>
</tr>
</tbody>
</table>

Sulphates in mine water flowing into the Budryk CM on levels 330 m and 540 m have very high values of isotopic composition, like those in the Bolesław Śmiały CM on level 530 m. Probably the mine waters of the Budryk CM dissolved the evaporites of the early Triassic - Roet.

Isotopic composition of sulphates in mine waters of the Chwałowice CM
The isotopic data and the concentrations and sulphates in mine waters of the Chwałowice CM are presented in Table 4.

Table 4 Isotopic composition and concentrations of sulphates in mine waters of the Chwałowice CM

<table>
<thead>
<tr>
<th>Number of sample</th>
<th>Sampling level</th>
<th>$\delta^{34}S$ [%e]</th>
<th>$\delta^{18}O$ [%e]</th>
<th>$SO_4^{2-}$ [mg/dm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>305 m (Miocene)</td>
<td>+20,25</td>
<td>+11,05</td>
<td>1800</td>
</tr>
<tr>
<td>2</td>
<td>390 m (Miocene)</td>
<td>+22,23</td>
<td>+11,10</td>
<td>850</td>
</tr>
<tr>
<td>3</td>
<td>550 m</td>
<td>+31,96</td>
<td>+15,64</td>
<td>790</td>
</tr>
<tr>
<td>4</td>
<td>550 m</td>
<td>+34,92</td>
<td>+17,36</td>
<td>1300</td>
</tr>
</tbody>
</table>

Sulphates in mine waters of the Chwałowice CM from the Miocene on levels 305 m and 390 m have $\delta^{34}S$ and $\delta^{18}O$ values characteristic for the sulphate minerals of the Badenian deposits. These sulphates are contained in salt bed of the Zawada Basin. In mine waters flowing on level 550 m the sulphates have very high values of isotopic composition. Probably there are from the evaporites of the early Triassic - Roet.

Isotopic composition of sulphates in mine waters of the Jankowice CM
The isotopic data and the concentrations of sulphates in mine waters of the Jankowice CM are presented in Table 5.

Table 5 Isotopic composition and concentrations of sulphates in mine waters of the Jankowicey CM

<table>
<thead>
<tr>
<th>Number of sample</th>
<th>Sampling level</th>
<th>$\delta^{34}S$ [%e]</th>
<th>$\delta^{18}O$ [%e]</th>
<th>$SO_4^{2-}$ [mg/dm$^3$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>565 m</td>
<td>+10,60</td>
<td>+1,86</td>
<td>830</td>
</tr>
<tr>
<td>2</td>
<td>565 m</td>
<td>+13,33</td>
<td>+6,17</td>
<td>235</td>
</tr>
<tr>
<td>3</td>
<td>565 m</td>
<td>+23,67</td>
<td>+6,89</td>
<td>45</td>
</tr>
</tbody>
</table>

The sulphates in mine waters flowing on the level 565 m of the Jankowice CM have different isotopic compositions. Probably these values are caused by the sulphides in oxidation and reduction processes.

Sulphates in the Žory and Krupiński coal mines
The natural mine waters flowing into the Žory and Krupiński coal mines do not contain sulphates. Waters are enriched in barium content.
Conclusions
Sulphates in the mine waters from the coal mines neighboring region of the Zawada Basin in the western and central part of the Upper Silesian Coal Basin have different isotopic compositions. In mine waters from the Miocene of the Chwałowice Coal Mine and from the Carboniferous formations in Dębienisko Coal Mine the sulphates have characteristic isotopic data of the evaporites in the marine Badenian deposits present in the different areas of Poland and in the salt bed of the Zawada Basin. Isotopic data of sulphates in mine waters from the Carboniferous formations of the Bolesław Śmiały, Budryk, Chwałowice, Jankowice are different. They are probably from the minerals of the early Triassic- Roet or were formed by the sulphides or the organic matter oxidation processes. Studies of the origin of sulphates confirmed the influence of salt bed of the Zawada Basin on the north-western side in mine waters of the Dębienisko Coal Mine. Based on this fact, the influence of salt bed from the Zawada Basin may also be observed in waters of the Paruszowiec region, where the potential sources of coal are present.

Acknowledgements
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References